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Highly Sensitive and Selective Sensing of H₂S Gas Using Precipitation and Impregnation-Made CuO/SnO₂ Thick Films

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Abstract

In this work, CuO-loaded tetragonal SnO₂ nanoparticles (CuO/SnO₂ NPs) were synthesized using precipitation/impregnation methods with varying Cu contents of 0–25 wt% and characterized for H₂S detection. The material phase, morphology, chemical composition, and specific surface area of NPs were evaluated using X-ray diffraction, transmission electron microscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and Brunauer–Emmett–Teller analysis. From gas-sensing data, the H₂S responses of SnO₂ NPs were greatly enhanced by CuO loading particularly at the optimal Cu content of 20 wt%. The 20 wt% CuO/SnO₂ sensor showed an excellent response of 1.36×10^5 toward 10 ppm H₂S and high H₂S selectivity against H₂, SO₂, CH₄, and C₂H₂ at a low optimum working temperature of 200 °C. In addition, the sensor provided fast response and a low detection limit of less than 0.15 ppm. The CuO–SnO₂ sensor could therefore be a potential candidate for H₂S detection in environmental applications.

Keywords: Precipitation/impregnation, CuO/SnO₂ thick films, Gas sensor, Sensing mechanism, Hydrogen sulfide

Background

Hydrogen sulfide (H₂S) is a highly toxic gas widely produced from several sources, such as manure fermentation plants, wastewater treatment systems, petroleum refineries, landfill sites, textile factories, stagnant water wells, extruded rubber industries, and other similar industrial facilities. H₂S can be adsorbed through human lungs, gastrointestinal regions, and normal skin. Its funky odor will freeze the sense of smell leading to immediate paralysis and mortality when its concentration exceeds its threshold limit value (TLV) of 10 ppm [1]. Therefore, it is compelling to develop an effective and low-cost gas sensor that can detect H₂S at sub-ppm concentrations with

high response, short response time, high selectivity and good stability.

Semiconducting metal oxides, such as zinc oxide (ZnO), tin dioxide (SnO₂), titanium dioxide (TiO₂) and nickel oxide (NiO), have been extensively studied for various gas-sensing applications [2–6]. Among them, tin dioxide (SnO₂) has been regarded as the most promising n-type metal oxide gas-sensing material due to its low cost, diverse gas response, ease of doping, high chemical stability, and wide range of working temperature from 100 to 600 °C [7–9]. In particular, it has been reported as one of the most attractive candidates for H₂S detection after the modification by doping with metallic dopants [10–18], loading with metal oxide nanoparticles [19–27], and forming nanocomposites with different metal oxide semiconductors [28, 29]. However, the H₂S-sensing performances of SnO₂ still need further improvements.

Copper Oxide (CuO) is a functional p-type metal oxide semiconductor with a moderate energy gap of

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1.2–2.0 eV, remarkable sensitivity and selectivity toward H_2S . CuO-loaded SnO_2 gas sensors have been extensively characterized toward H_2S as presented in Table 1. CuO dopants provides relatively high enhancement of H_2S response and selectivity for SnO_2 sensors [19–27]. The H_2S -sensing performances also depend substantially on the synthesis method and the form of metal oxide materials. From the table, recent reports CuO/ SnO_2 sensors are mostly in thick-film and thin-film forms, which offer similarly competitive H_2S -sensing performances depending on synthesis method and preparation parameters. Between them, thick-film sensors are more preferred in practical applications due to their much lower production cost. Hence, it is compelling to investigate the H_2S -sensing properties of thick-film CuO/ SnO_2 materials prepared by other advanced techniques.

Precipitation and impregnation are attractive methods for production of thick-film nanocomposite materials because of ability to form diverse nanostructures, low processing temperature, and low cost. Some CuO-loaded SnO_2 nanomaterials synthesized by precipitation with NH_3 precipitant and impregnation were studied for H_2S gas-sensing. However, the reported results still offered only modest response at high H_2S concentrations due possibly to large particle sizes [28]. Herein, precipitated SnO_2 nanoparticles (NPs) were prepared using NaOH

as a precipitant and impregnated with CuO at over a wide range of Cu contents to attain small nanoparticles and large responses at relatively low H_2S concentrations. Thick-film sensors were fabricated by spin coating powder paste of synthesized CuO/ SnO_2 nanoparticles and the effects of CuO loading level on H_2S -sensing properties were explained based on CuO/ SnO_2 heterojunctions.

Methods

Synthesis and Characterization of Nanoparticles

All chemicals with analytical grade were used directly without additional purification. Tin (IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) as a tin source was dissolved in deionized (DI) water under constant stirring to obtain the 0.1 M aqueous solution. An appropriate volume of 0.1 M sodium hydroxide (NaOH) aqueous solution was slowly dropped onto the SnCl_4 solution under vigorous stirring until white slurry appeared at the pH of 11. The slurry was washed thoroughly with DI water several times under centrifugation to remove chloride residues from the precipitate. The resulting precipitate was subsequently dried at 80 °C for 10 h in an oven and the obtained particles were calcined for 2 h at 600 °C at a heating rate of 10 °C/min. To impregnate CuO onto SnO_2 nanoparticles, 0.872 g of copper (II) acetate hydrate (98%; Aldrich) was dissolved in 30 mL of ethanol under

Table 1 A summary of H_2S response of metal-loaded SnO_2 and CuO/ SnO_2 nanomaterials prepared by various methods

Materials	Form	Technical used	Gas conc. (ppm)/ Temp (°C)	H_2S Response	Refs
3.0 mol% Ag– SnO_2	Thick film	Spray pyrolysis	450/100	1.38	[10]
0.1 wt% V– SnO_2	Thick film	Flame spray pyrolysis and spin coating	10/350	2.27×10^3	[11]
0.5 wt% Mo– SnO_2	Thick film	Flame spray pyrolysis and spin coating	10/250	≈ 105	[12]
Sb– SnO_2 nanoribbons	Thin film	Thermal evaporation	100/150	≈ 55	[13]
0.64 at% Fe– SnO_2	Thin film	Rheotaxial grown and Thermal oxidation	10/225	14.5	[14]
Cu-doped SnO_2	Thick film	Ultrasonic spray pyrolysis	95.9/100	7.24×10^3	[15]
2mol% Cu– SnO_2	Thick film	Hydrothermal and drip coating	300/300	40	[16]
Cu– SnO_2 nanowires	Thin film	Thermal evaporation	10/150	5×10^5	[17]
1 at% Cu– SnO_2	Thick film	Electrostatic sprayed	10/100	2.5×10^3	[18]
SnO_2 /CuO islands	Thin film	Sputtering	5/250	128	[19]
CuO-loaded SnO_2	Thick film	Ultrasonic spray pyrolysis	1/300	22.4	[20]
CuO/ SnO_2	Thin film	Chemical vapour deposition	10/250	26.3	[21]
3 vol% CuO– SnO_2	Thin film	Pulsed laser deposition	20/140	2.7×10^4	[22]
CuO-loaded SnO_2	Thin film	Electrospinning	10/300	1.98×10^4	[23]
5 mol% CuO/ SnO_2	Thin film	Co-dissolution and electrospinning	1/200	≈ 23	[24]
SnO_2 –CuO	Thin film	Sputtering	20/150	8×10^3	[25]
CuO– SnO_2	Thin film	Pulsed laser deposition	20/100	2.3×10^3	[26]
CuO– SnO_2 nanowire	Thick film	Thermal evaporation	20/300	809	[27]
CuO– SnO_2	Thick film	Precipitation/Impregnation and drop coating	50/200	6.7	[28]
20 wt% CuO/ SnO_2	Thick film	Precipitation/Impregnation and spin coating	10/200 10/150	1.359×10^5 3.1×10^4	This work

vigorous agitation. The solution was then dropped onto 0.5 g of SnO₂ NPs with varying Cu concentrations from 5 to 25 wt%. Next, the suspension was continuously stirred until turning into homogeneous slurry and baked at 60 °C for 2 h in an oven. The resulting powders were annealed for 4 h at 300 °C at a heating rate of 10 °C/min.

The structural characteristics of NPs were evaluated using X-ray diffraction (XRD) with a Cu *K* α ($\lambda = 1.54056$ Å) X-ray source. The surface morphology and elemental distributions of NPs were examined using high-resolution scanning transmission electron microscopes (HR-TEM). The oxidation states of materials were studied using X-ray photoelectron spectroscopy (XPS) with an Al-*K* α (1486.8 eV) X-ray source. The specific surface area of the NPs was measured using a nitrogen-adsorption analyser with Brunauer–Emmett–Teller analysis (SSA_{BET}).

Fabrication and Characterization of Gas Sensor

To fabricate SnO₂ and 5–25 wt% CuO/SnO₂ sensors, 60 mg of powder was thoroughly mixed with an α -terpineol (Aldrich, 90%)-based vehicle containing ethyl cellulose (30–70 mPa s, Fluka) to produce a homogeneous paste. Next, a sensing film was deposited on an alumina substrate ($0.40 \times 0.55 \times 0.04$ cm³) with prepatterned interdigitated gold electrodes (0.24 cm \times 0.5 cm) by spin coating of the paste at 700 rpm for 10 s and at 3000 rpm for 30 s. The 200-nm-thick interdigitated Au electrodes were deposited on alumina substrates by a sputtering process with argon gas at a pressure of 3×10^{-3} mbar. The interdigit spacing, width, and length were 100 μ m, 100 μ m, and 0.24 cm, respectively. The resulting sensors as illustrated in Fig. 1 were annealed for 2 h at 450 °C at a ramping rate of 4 °C/min to eliminate organic components from the sensing layers. The microstructures of sensing films were characterized using field-emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray analysis (EDS).

Gas Sensing Measurement

The sensor characteristics toward H₂S in the concentration range of 0.15–10 ppm was measured in a home-made sealed stainless-steel test chamber with an active volume of 0.5 L (Fig. 1). An external Ni/Cr heater operated with a computer-controlled power supply was used to control the working temperature ranging from 150 to 350 °C. The selectivity properties were evaluated against H₂, SO₂, CH₄ and C₂H₂. At a given working temperature, the sensors were initially settled in synthetic dry air for 10 min to obtain a steady resistance in air. Next, the dry air was mixed with a target gas sample to a desired gas concentration at a fixed total flow rate (2 L/min) using computerized multichannel mass flow controllers (Brook

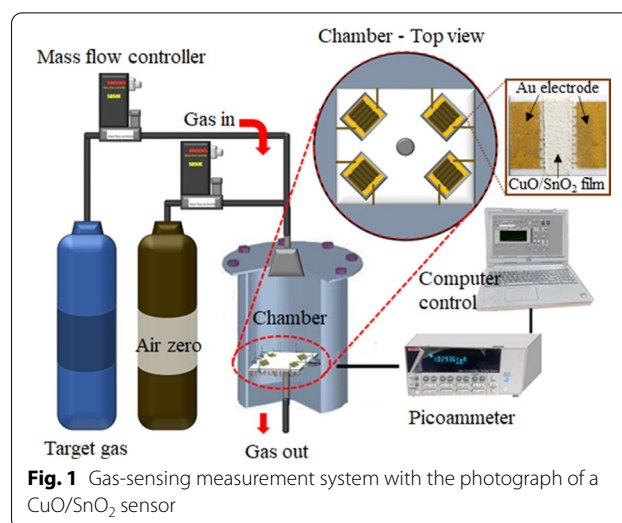


Fig. 1 Gas-sensing measurement system with the photograph of a CuO/SnO₂ sensor

Instruments model 5850E). Each gas sample was applied to the sensors for 25 min and the dry air was resumed for 45 min. The sensor resistance was measured by the amperometric method at a bias of 10 V DC using a picoammeter (Kiethley model 6487). The performances of sensors with various Cu concentrations were characterized in terms of gas response, response time, selectivity, and stability. The gas response (*S*) was expressed as $S = R_a/R_g$ for a reducing gas (H₂S, H₂, CH₄, SO₂ and C₂H₂), where *R_a* and *R_g* were the sensor resistance in air before and after exposure to a target gas, respectively. The response time (*t_{res}*) was the time taken to attain 90% of a steady-state response signal upon exposure to a target gas.

Results and Discussion

Structural Characteristics of Particles and Sensing Film

XRD patterns of CuO, SnO₂, and 5–25 wt% CuO/SnO₂ NPs are displayed in Fig. 2. The sharp diffraction peaks indicate the crystalline characteristic of all NPs. The diffraction patterns of SnO₂ and CuO correspond to tetragonal and monoclinic structures according to JCPDS files no 41-1445 and 45-0937, respectively. The SnO₂ powder exhibits three main peaks, while the CuO powder displays two distinct major peaks. The spectra for the 5–25 wt% CuO/SnO₂ NPs show the secondary CuO peaks of (002) and (111) planes together with the main SnO₂ peaks of (111), (101) and (211) planes, demonstrating the coexistence of CuO and SnO₂ phases. The mean crystallite sizes (*d*) of CuO/SnO₂ NPs were determined using Scherrer's equation ($d = K\lambda/(\beta \cos \theta)$) where *K* is the geometric factor of 0.89 for spherical particles, λ is the X-ray wavelength and β is the full width at half maximum of an XRD peak at the angle,

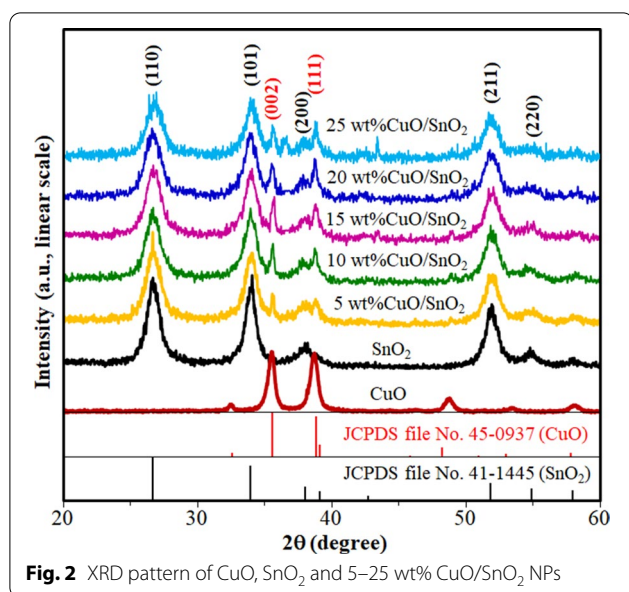


Fig. 2 XRD pattern of CuO, SnO₂ and 5–25 wt% CuO/SnO₂ NPs

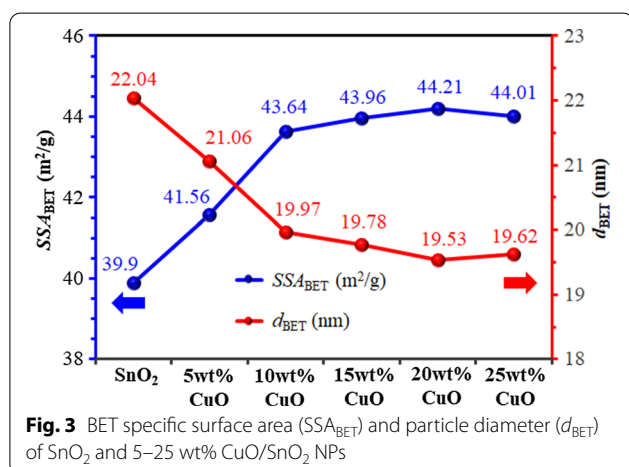


Fig. 3 BET specific surface area (SSA_{BET}) and particle diameter (d_{BET}) of SnO₂ and 5–25 wt% CuO/SnO₂ NPs

θ . The mean crystallite diameter of unloaded SnO₂ is estimated to be 10 nm, while that of 20 wt% CuO/SnO₂ NPs is relatively small at 7 nm. The result indicates the inhibition of grain growth due to CuO loading on SnO₂ NPs. The chemical compositions and oxidation states of CuO and SnO nanoparticles will be evaluated further by EDX and XPS analyses.

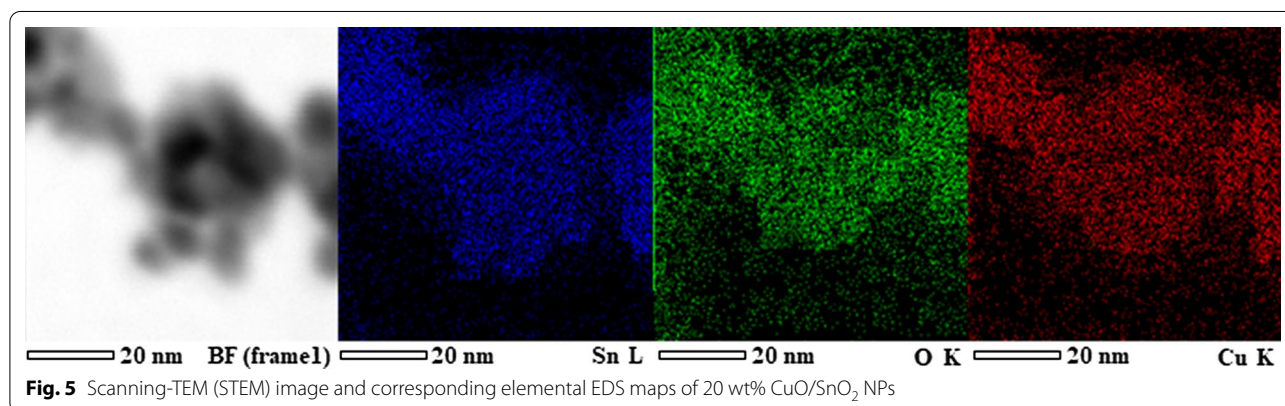
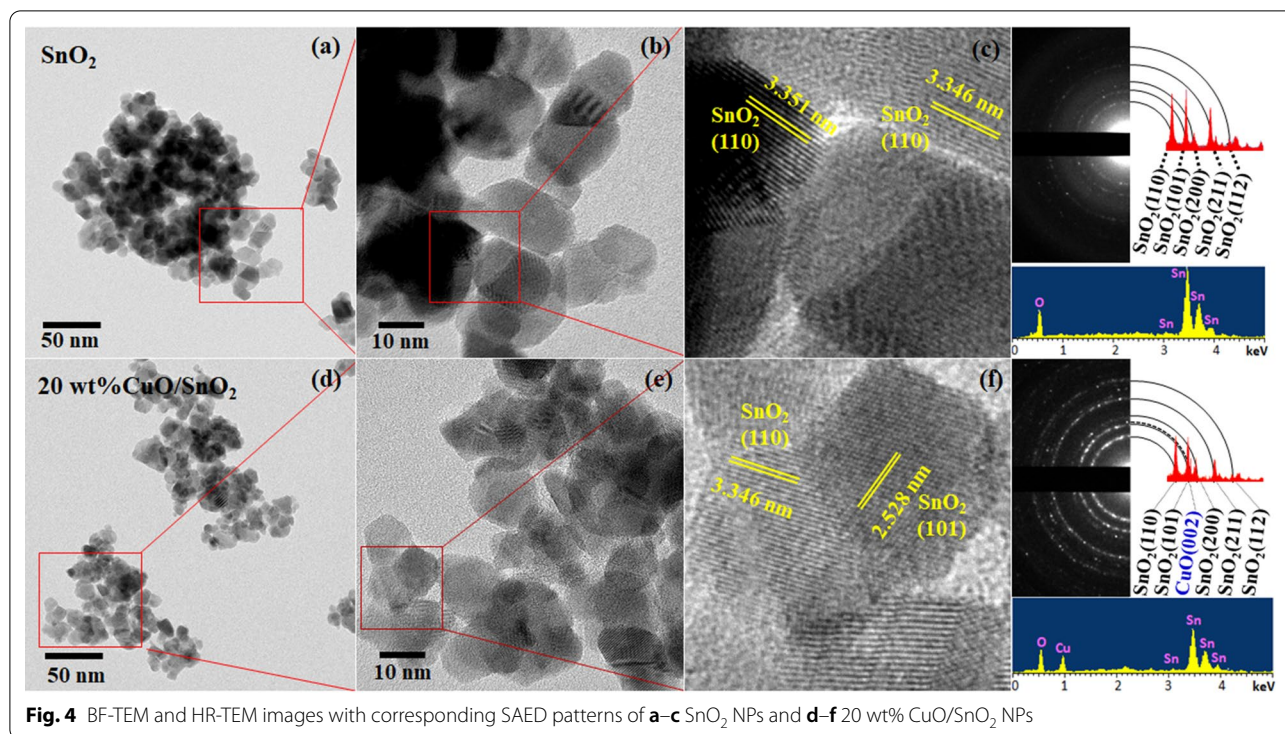
BET specific surface areas (SSA_{BET}) and particle diameters (d_{BET}) of SnO₂ and 5–25 wt% CuO/SnO₂ NPs are shown in Fig. 3. SSA_{BET} of CuO/SnO₂ NPs substantially increases from 39.9 to 44.21 m²/g, while the d_{BET} reduces accordingly from 22.04 to 19.53 nm as the CuO content rises from 0 to 20 wt%. As the Cu content increases further to 25 wt%, SSA_{BET} decreases slightly to 44.01 m²/g and d_{BET} increases to 19.62 nm. The

results agree with the XRD analysis of crystallite size. The influence of CuO loading level on SSA_{BET} may be attribute to the inclusion of smaller CuO NPs produced by impregnation. The CuO NPs may act as separators to inhibit self-coagulation among SnO₂ NPs, resulting in the substantial increment of the effective surface area.

Figure 4 shows typical surface morphologies of coprecipitation/ impregnation synthesized SnO₂ and 20 wt% CuO/SnO₂ NPs. The BF-TEM images show that most SnO₂ particles exhibit spheroidal shapes with different diameters ranging from 5 to 20 nm. After CuO loading, the diameters of SnO₂ NPs tend to be smaller but the secondary phase of CuO cannot be clearly identified (Fig. 4d–f). The related SAED patterns display dotted ring features of polycrystalline tetragonal SnO₂ structures with main diffraction rings corresponding to (110), (101), (200), (211) and (112) planes of SnO₂ as well as (002) plane of CuO in agreement the XRD analysis. The rings related to CuO were quite obscure due likely to weak diffraction signal from very small CuO secondary phase. Correspondingly, the HR-TEM images show lattice fringes on nanoparticles mainly associated with the planes of SnO₂ crystals. The secondary CuO phase structures cannot be observed in HR-TEM image due possibly to their very small sizes beyond the resolution of the TEM instrument.

Scanning transmission electron microscopy (STEM) and high-resolution EDS mapping analysis were employed to investigate the distributions of CuO in 20 wt% CuO/SnO₂ NPs as presented in Fig. 5. The STEM image illustrates a cluster of roughly round nanoparticles with diameters in the range of 5–15 nm in agreement with the TEM images but with relatively low image resolution due to scanning aberration. The corresponding EDS maps of Sn, O, and Cu elements demonstrate the detailed distribution of these species on various SnO₂ nanoparticles in the selected area. Apparently, Cu species are widely distributed on particles with similar density to Sn and O species. The results suggest that the CuO secondary nanoparticles are present and closely distributed on SnO₂ surfaces forming distributed CuO–SnO₂ junctions within the CuO/SnO₂ composite. However, the particles and related junctions are very small at molecular scales so that they cannot be exactly discerned by the TEM/STEM characterizations.

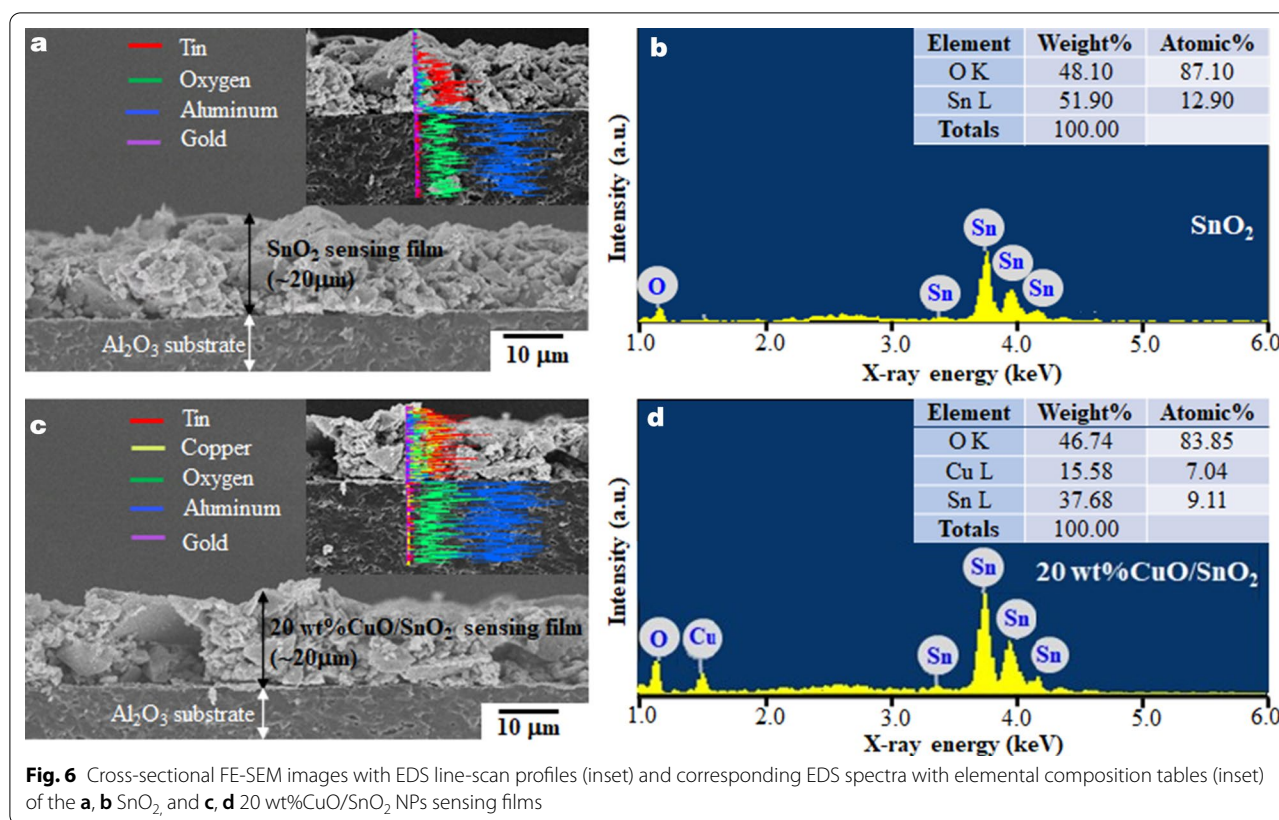
Figure 6 illustrates the cross-sectional morphologies and chemical compositions of SnO₂ and 20 wt% CuO/SnO₂ films. Both layers are approximately 20 μ m thick and similarly comprise agglomerated particles on solid-textured substrates. The elemental compositions of SnO₂ and 20 wt% CuO/SnO₂ are listed in the inset tables of Fig. 5b, d. It reveals that the atomic contents of Sn and O of SnO₂ NPs are lower than the expected values (33:67)



of stoichiometric SnO_2 . With 20 wt% CuO loading, a Cu peak appears with a high Cu content of ~ 15.6 wt% or 7.04 at%, which is still smaller than that of Sn . Additionally, the Cu content from five different areas is found to vary from 14 to 18 wt%, indicating some variation of chemical composition within the film. Therefore, CuO loading by impregnation does not markedly influence particle morphologies but considerably changes the elemental composition.

Figure 7 presents the oxidation states of elements in SnO_2 and 20 wt% CuO/SnO_2 NPs. The XPS survey spectrum of SnO_2 reveals the presence of C , O and Sn , while that of 20 wt% CuO/SnO_2 demonstrates the existence

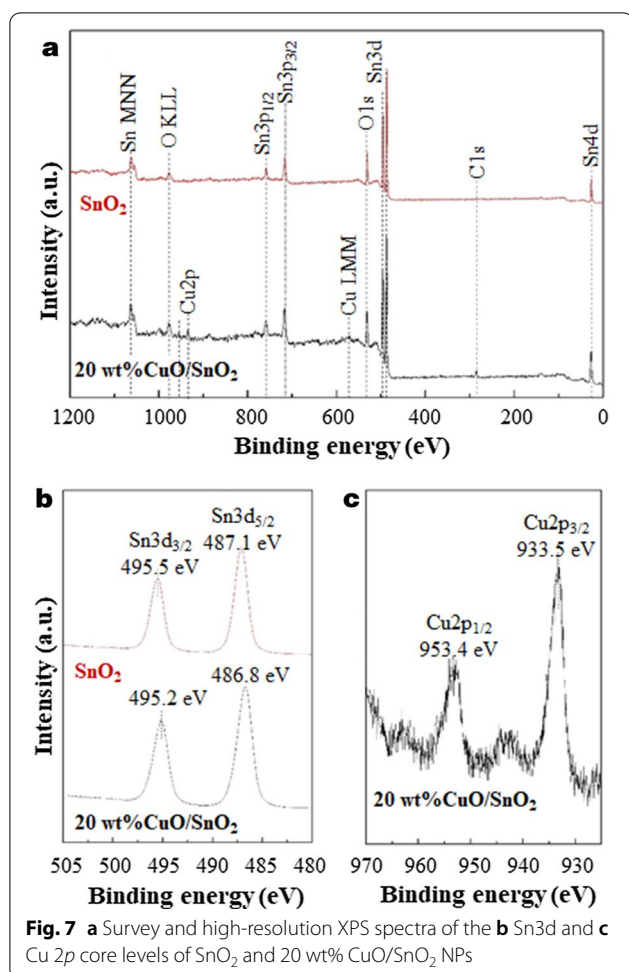
of C , O , Sn and Cu . The results confirm the formation of CuO/SnO_2 composites with typical organic/carbon contaminations on surfaces. For Sn element, the $\text{Sn}3d_{5/2}$ and $\text{Sn}3d_{3/2}$ doublet peaks of SnO_2 and 20 wt% CuO/SnO_2 NPs are similarly observed at the binding energies of 486.8–487.1 eV and 495.2–495.5 eV, respectively. The peak locations can be assigned to the Sn^{4+} oxidation state of SnO_2 [29]. In the case of 20 wt% CuO/SnO_2 NPs, the $\text{Cu}2p$ core levels comprise $\text{Cu}2p_{3/2}$ and $\text{Cu}2p_{1/2}$ peaks centred at 933.5 eV and 953.4 eV along with the satellite peaks at ~ 942.9 and ~ 964.2 eV, corresponding to the Cu^{2+} oxidation state of CuO [30]. The observed oxidation states affirm the coexistence of CuO and SnO_2 structures.



Gas-Sensing Characteristics

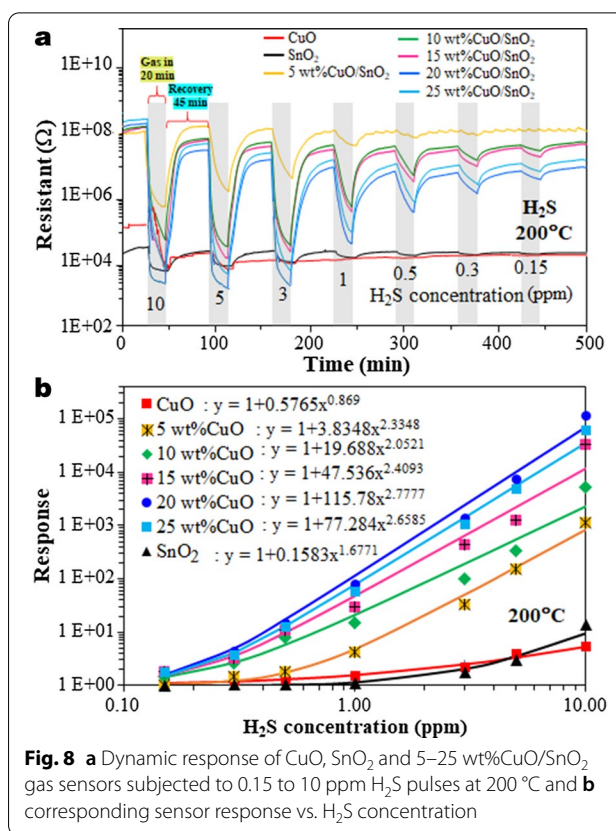
Figure 8a displays the changes in resistance of CuO , SnO_2 and 5–25 wt% CuO/SnO_2 films subjected to H_2S pulses with varying concentrations from 0.15 to 10 ppm at a working temperature of 200 $^\circ\text{C}$. The resistance in air of SnO_2 film increases by more than two orders of magnitude after loading CuO with 5–25 wt% contents. Additionally, it is observed that the baseline resistances of various CuO/SnO_2 sensors are not very different and only tend to increase slightly with increasing CuO loading level. To identify whether the resistance is changed due to the film geometry or material related properties, the film resistivity was additionally measured by the well-known four-probe method using 4-stripe Au/Cr electrodes with an interelectrode spacing of 100 μm and a bias current of 0.1 μA . The measured average resistivity values of CuO , SnO_2 , and 5–25 wt% CuO/SnO_2 films in air at 350 $^\circ\text{C}$ are $\sim 8.1 \times 10^3$, 2.1×10^4 and $7.4 \times 10^7 - 1.8 \times 10^8 \Omega \text{ cm}$, respectively. The results confirm significant differences in resistivity among the three sets of materials and the similarities in resistivity among 5–25 wt% CuO/SnO_2 films. This behavior may be explained based on two effects including the percolation breaking of aggregated SnO_2 nanoparticles due to CuO secondary nanoparticles and the formation of CuO/SnO_2 (p–n) heterojunctions. The

TEM/HR-TEM/STEM data suggest that CuO secondary nanoparticles may be formed surrounding the SnO_2 nanoparticles, thus breaking the percolation of agglomerated SnO_2 particles and forcing most conduction paths to be across the CuO nanoparticles. In addition, the formation of CuO/SnO_2 heterojunctions may induce carrier depletion regions throughout secondary CuO nanoparticles due to the work function difference, creating highly resistive conduction paths. Thus, an addition of CuO to SnO_2 particles at the level above the minimum value required to break the percolation of SnO_2 particles will cause a large increase of resistance as fully depleted CuO particles block electrical conduction. The lowest Cu content in this study of 5% is quite substantial and thus likely to exceed the percolation breaking threshold. Further addition of CuO will only slightly increase the resistance since the electrical conduction via fully depleted CuO is already nearly minimal. Other effects including particle/grain sizes, film thickness, electrode separation, and electrode contact may be neglected since they are not greatly changed according to the structural characterization results. Upon exposure to H_2S , the sensor resistances decrease rapidly before recovering to the baseline levels after the resumption of dry air, confirming a typical n-type sensing characteristic. Interestingly, the baseline



resistance of CuO sensor considerably drifts downward after several H₂S pulses in contrast to the SnO₂ sensor that shows insignificant baseline drift. In the case of CuO/SnO₂ sensors, the baseline drift tends to increase with increasing Cu content. These behaviors may be related to the slow and incomplete CuO–CuS transformative reactions to be further discussed in Sect. 3.3.

The corresponding sensor response plotted versus H₂S concentration at 200 °C is shown in Fig. 8b. All sensor responses increase monotonically with increasing H₂S concentration. The response characteristics of all sensors conform well to the power law according to the equations as displayed along with the inset labels in Fig. 8b. The power-law exponent of CuO is close to 1, while that of SnO₂ sensors is around 1.5 and those of CuO-loaded SnO₂ sensors are larger than 2, suggesting differences in H₂S reaction mechanisms on the surfaces of these materials [31]. Furthermore, the sensor response increases greatly as the CuO content increases from 0 to 20 wt% before slightly declining at a higher CuO content of 25 wt% and the 20 wt% CuO/



SnO₂ sensor offers the highest response of 1.36×10^5 to 10 ppm H₂S at 200 °C. Moreover, it exhibits decent responses of ~2, 5, 20 and 230 at the lower H₂S concentrations of 0.15, 0.3, 0.5 and 1 ppm, respectively. The excellent performances of 20 wt% CuO/SnO₂ sensor may be attributed to the increase of specific surface area due to CuO loading and the formation of CuO/SnO₂ heterojunctions to be further discussed in the next section.

Figure 9 presents the plot of the response versus working temperature of unloaded and CuO-loaded SnO₂ sensors at a H₂S concentration of 10 ppm. The H₂S responses of CuO/SnO₂ NPs sensors increase significantly with the increasing temperature from 150 to 200 °C and then reduce rapidly when the temperature further rises. Hence, 200 °C is the optimal working temperature of the CuO-loaded SnO₂ sensors. Specifically, the optimal 20 wt% CuO/SnO₂ sensor gives the highest response of 1.36×10^5 , which is much higher than those of other sensors at 200 °C. The optimal working temperature of 200 °C corresponds to the temperature that maximizes the H₂S adsorption rate relative to desorption rate of CuO/SnO₂ surfaces. Furthermore, 5–25 wt% CuO/SnO₂ sensors display a lower optimal working temperature than that of SnO₂ sensor (250 °C). The relatively low

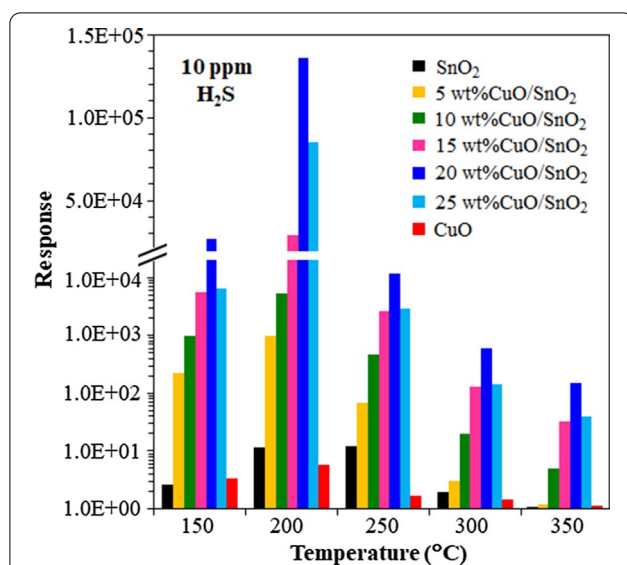


Fig. 9 Effect of working temperature on response to 10 ppm H_2S of CuO , SnO_2 and 5–25 wt% CuO/SnO_2 sensors

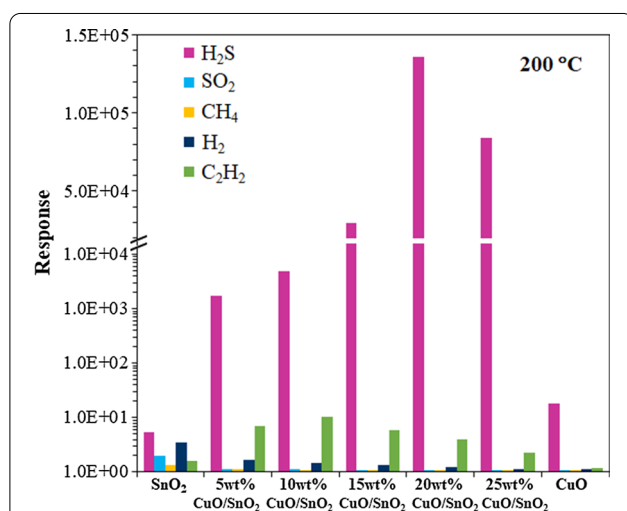


Fig. 10 Responses of CuO , SnO_2 and 5–25 wt% CuO/SnO_2 sensors toward H_2S (10 ppm), SO_2 (200 ppm), CH_4 (1000 ppm), H_2 (1000 ppm) and C_2H_2 (1000 ppm) at 200 °C

optimal working temperature will be subsequently elucidated by CuO loading effects.

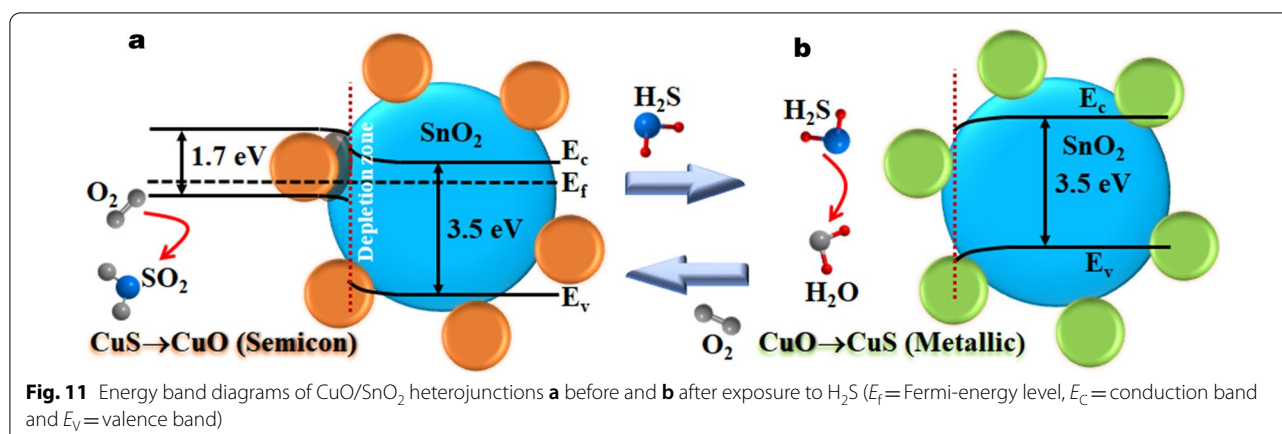
Figure 10 summarizes the H_2S selectivity of 0–25 wt% CuO/SnO_2 sensors against SO_2 , H_2 , CH_4 and C_2H_2 . This type of sensor exhibits the highest H_2S selectivity, i.e., more than three orders of magnitude higher H_2S response than those of other gases. The data prove that CuO is the catalyst that selectively accelerates the reaction with H_2S . The selectivity behavior may also be attributed to the increase of active sites for H_2S adsorption due to the

highest specific surface area of 20 wt% CuO/SnO_2 NPs. The enhancements for other tested gases are not significant due probably to relatively weak interactions between gas molecules and 20 wt% CuO/SnO_2 NPs. The attained H_2S responses of 20 wt% CuO/SnO_2 sensors are substantially better than those of many other metal-loaded SnO_2 and CuO -loaded SnO_2 sensors made by distinct techniques as listed in Table 1. However, the achieved optimal working temperature of 200 °C is higher than the values of some reports at 100–150 °C. The lower working temperature is generally preferred in practical applications. Nevertheless, the 20 wt% CuO/SnO_2 sensor may operate at a lower working temperature of 150 °C where the sensor still exhibits a high response of 3.1×10^4 to 10 ppm H_2S (Fig. 9), which is also higher than the response values of other sensors reported in Table 1. Therefore, the CuO -loaded SnO_2 sensor is a highly promising candidate for H_2S sensing due to its high H_2S response, high H_2S selectivity and low working temperature.

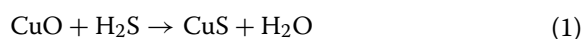
Finally, the stability, repeatability, and reproducibility of CuO/SnO_2 sensors were evaluated from four samples produced in the same batch. All sensors exhibited good stability with less than 15% drift in sensor response over 1 month under the same operating conditions. Moreover, each sensor showed good repeatability with less than 12% response variation from 8 repeated measurements. In addition, four sensors from the same batch were found to have fair response variation of less than 26% evaluated under the same test condition.

Gas-Sensing Mechanisms

The characterization results suggest the formation of CuO/SnO_2 composite comprising very small CuO species on SnO_2 nanoparticles. Thus, the mechanisms for electrical response of CuO/SnO_2 sensing films toward H_2S may be described based on the composite junction theory of p-n junctions at the contacts between p-type CuO and n-type SnO_2 as depicted in Fig. 11. For undoped SnO_2 , chemisorbed oxygen species (O^-) are formed resulting in the creation of depletion regions on surface at a moderate temperature. Upon exposure to H_2S , H_2S molecules interact with adsorbed oxygen species on SnO_2 surface ($\text{H}_2\text{S} + 3\text{O}^- \rightarrow \text{H}_2\text{O} + \text{SO}_2 + \text{e}^-$), releasing electrons to SnO_2 conduction band and reducing the sensor resistance. At a low working temperature of 200 °C, the concentration of oxygen species is very low, leading to a low reaction rate and a low H_2S response. With CuO loading, additional depletion regions will be formed at various p-n junctions around the surface of SnO_2 nanoparticles. In addition, carriers in secondary CuO nanoparticles, which can break percolation of aggregated SnO_2 nanoparticles, may be fully depleted, resulting in a high electrical resistance in air. In ambient with H_2S , the gas molecules can

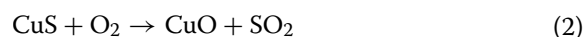


additionally react with the catalytic CuO NPs, leading to the creation of copper sulfide (CuS) via the reaction (Eq. 1) [26]:



CuS is more conductive than CuO, leading to lower potential barriers at depletion regions around the interfaces. The induction of metallic CuS is equivalent to the injection of free electrons into the p-type material (CuO), making it less p-type. This encourages the electron transfer from CuS to SnO₂, resulting in additional decrease of depletion width and increase of the electrical conductance of SnO₂. The decrease of resistance due to the formation of CuS is much larger than the reduction due to the reducing reaction with oxygen species due to transfer of more electrons from CuS. At low CuO contents, there are relatively few and small CuO nanoparticles that are fully transformed into CuS surrounding SnO₂ particles. It will provide a limited amount of electrons to SnO₂ due to relatively few heterojunctions, resulting in small reduction of depletion region widths in SnO₂ and small resistance drop upon H₂S exposure. As the CuO content increases, the numbers of transformed CuS nanoparticles and heterojunctions increase, leading to an increased number of conduction paths through CuS as well as much reduced SnO₂ depletion region widths and thus a higher resistance drop that can be achieved after H₂S exposure. However, CuO particles may coalesce into large ones and the number of CuO/SnO₂ heterojunctions becomes lower at very high CuO content (> 20 wt%). The large CuO particles will not be fully transformed to CuS due to limited reaction depth with H₂S and the depletion regions in CuO cores remain, limiting the conduction through CuO and reducing attainable resistance drop. In the case of CuO, the response is low despite the formation of CuS because the resistance of CuO is already

low and is not much higher than that of CuS [20]. After H₂S in atmosphere extinguishes, the electrical resistance returns to its original values as CuS can be reoxidized to CuO in air at an elevated temperature according to the reaction (Eq. 2) [26]:



The oxidation of CuS is slow at a low working temperature. As the increase of working temperature, the oxidation rate increases and lead to the increase of recovery rate. Since the CuS–CuO transformative reaction (Eq. (2)) is slower than the CuO–CuS one (Eq. (1)) at this working temperature, residual CuS materials can remain after subjecting CuO to several H₂S pulses. This results in a substantial downward baseline drift of CuO sensor and the increase of baseline drift with increasing Cu content of CuO/SnO₂ sensors as previously observed in Fig. 8a. However, there is an exception in the case of 5 wt% CuO/SnO₂ sensor, which exhibits a small upward drift of baseline resistance after the first pulse. It may occur because the sensor did not fully reach the steady state before applying the first pulse leading to some upward recovery owing to oxidation in air while the drift due to CuS–CuO transformation at this low Cu content is relatively small due to a low residual CuS content. At higher Cu contents, the downward drifts due to residual CuS are large and overwhelm the small upward recovery. The baseline drift considerably reduces the validity, repeatability and stability of sensor response of CuO/SnO₂ as the response to a subsequent H₂S pulse is affected by the residual CuS concentration after the previous H₂S exposure leading to negative deviations from the ideal response behavior. Thus, the calculated responses of the CuO/SnO₂ sensors especially with high Cu contents in Fig. 8b are lower the theoretical values under no residual CuS condition. The problems can be reduced by increasing the working temperature. Thus, the sensors may operate above

the optimal working temperature at 250 °C when the drift is low, and response is still high. CuS structure can be formed at 103 °C and will be transformed into Cu₂S, a less conductive ionic conductor, at the temperature above 220 °C [26]. Consequently, the sensor response of CuO/SnO₂ NPs decreases when the temperature rises above 200 °C. The observed high H₂S selectivity against SO₂, H₂, CH₄ and C₂H₂ can also be explained in relation to the working temperature. At the optimal working temperature of 200 °C, the rate of CuO–CuS transformation is high, while the reducing reaction rates of SO₂, H₂, CH₄ and C₂H₂ are very low because these reactions require the chemisorbed oxygen species whose density is still very low at this working temperature.

Conclusions

0–25 wt% CuO/SnO₂ NPs were fabricated using the precipitation and impregnation method. XRD, BET, TEM, SEM, EDS and XPS data suggested the loading of very small CuO nanoparticles on larger SnO₂ NPs. The gas-sensing results demonstrated that CuO loading greatly enhanced the H₂S response of SnO₂ NPs with an optimal Cu content of 20 wt%. The 20 wt%CuO/SnO₂ sensor can perceive low-ppm H₂S concentrations with ultra-high responses (1.4×10^5 at 10 ppm), short response times (35 s), fair recovery times (a few minutes), very high H₂S selectivity against SO₂, CH₄, H₂ and C₂H₂ and good stability. They could also offer a wide detection range (0.15–10 ppm) when compared with the unloaded one (3–10 ppm). Therefore, the CuO/SnO₂ sensors synthesized by precipitation and impregnation could be a promising candidate for H₂S detection in environmental applications.

Abbreviations

NPs: Nanoparticles; XRD: X-ray diffraction; HR-TEM: High-resolution transmission electron microscopy; FE-SEM: Field-emission scanning electron microscopy; EDX: Energy-dispersive X-ray spectroscopy; AFM: Atomic force microscopy; BET: Brunauer–Emmett–Teller; SSA_{BET}: Specific surface area; XPS: X-ray photoelectron spectroscopy.

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Authors' contributions

V.K and P.L carried out the experiments, acquired the original data, participated in the sequence alignment, fabricated the devices, performed measurements and wrote the manuscript. A.W, A.T and S.P assisted in processing the data and figures. K.J and N.C helped measure the devices. All the authors read and approved the final manuscript.

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Availability of data and materials

The datasets supporting the conclusions of this article are included in the article.

Declarations

Competing interests

The authors declare that they have no competing interests.

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